

Gennady Zaikov

WILLIAM H. STARNES, JR.: HALF A CENTURY IN SCIENCE

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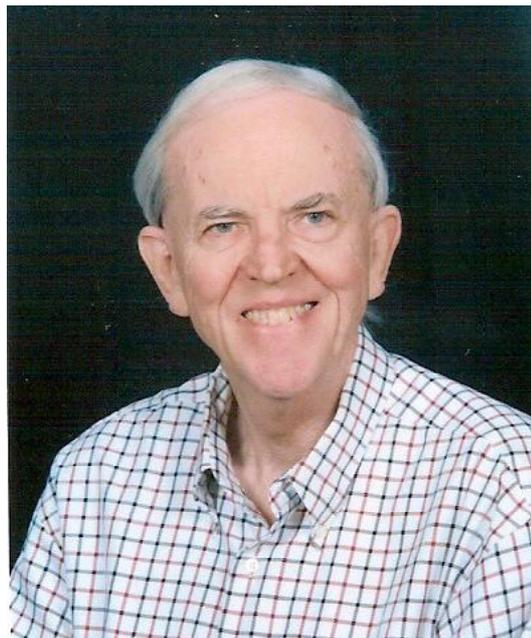
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William H. (Bill) Starnes, Jr., was born in Knoxville, Tennessee, on December 2, 1934. His formative years were spent in Ewing, Virginia, where his parents, Edna O. Starnes and William H. Starnes, Sr., were educators in the local public schools. His father headed the Agriculture program of Thomas Walker High School and was noted for his advocacy of scientific farming methods.

After graduating from Thomas Walker in 1950, Bill Starnes entered Union College in Barbourville, Kentucky, with support from a high school valedictorian scholarship. There he took courses in organic and general chemistry that were taught by an inspiring young professor, Dr. Rupert B. Hurley. As a result of his stimulating interaction with Hurley, Starnes decided to embark on a chemical career. At Union he also served for a year as Editor-in-Chief of the college newspaper, there he got an experience that solidified his lifelong interest in expository and creative writing.

In 1952, Starnes transferred to Virginia Polytechnic Institute (now known as Virginia Tech), where he received the B. S. degree in Chemistry with Honors in 1955 and graduated at the head of the Chemistry class. There, working under the direction of Dr. Frank A. Vingiello, he completed his first research project. It dealt with the chlorination of 9-methylanthracene and was the subject of his B.S. thesis.

Starnes entered Duke University in the fall of 1955 but left in good standing in the spring of 1956 and entered the graduate Chemistry program of the Georgia Institute of Technology (Georgia Tech) in the fall semester of that year. He found this opportunity to be especially attractive because of the major research emphasis at Georgia Tech on physical organic chemistry. Working there in the laboratory of Dr. James A. Stanfield with support from the U. S. Public Health Service and Predoctoral Fellowships awarded by the National Science Foundation, he began synthetic and mechanistic studies on substances that were thought to be spiroaminobarbituric acids. His research soon showed, however, that the compounds were unusable because they were actually not barbituric acids at all! Undeterred, he proceeded to develop an authentic method of synthesis for some of the needed materials. Then he studied the basic hydrolysis of barbituric acids, in general, and discovered a correlation



between the hydrolytic stability *in vitro* and the hypnotic potency *in vivo* of this class of medicinals. His thesis describing this research received the annual M. A. Ferst Award for the best doctoral dissertation (among all disciplines) at Georgia Tech and led to the Ph. D. degree in Chemistry for Starnes in 1960. However, the structures of the compounds which he studied originally remained a mystery until quite recently (see below).

Later in 1960, Starnes accepted a research position at the Baytown, Texas, laboratories of the Humble Oil and Refining Company (subsequently a part of Esso Research and now Exxon Mobil). This facility is well-known in scientific circles as the birthplace of chemical ionization mass spectroscopy. There Starnes rose through the ranks to the level of Research Associate and served for a time as Head of the Polymer Additives Section, whose principal mission was to develop stabilizers and other additives for polypropylene, a major company product. During this period, he delved extensively into mechanistic free-radical chemistry, which became one of his lifelong interests, and conducted research on liquid-phase air oxidation, organic peroxides, phenolic antioxidants, quinone methides,

organophosphorus chemistry, lead tetraacetate oxidation, organic photochemistry, coal liquefaction, and other topics of significant interest at that time. In the course of this work, he (a) discovered a decarboxylation process that forms aryl radicals from benzoic acids during metal-catalyzed air oxidations, (b) developed an economical synthesis for a new trisphenol antioxidant with an exceptional activity at high temperatures, (c) discovered chlorophenol antioxidants that are extraordinarily effective in the presence of metals because they are autosynergistic in such systems, (d) established a detailed free-radical mechanism for the lead tetraacetate oxidation of monohydric alcohols, and (e) obtained the first conclusive evidence for the existence of aliphatic acyloxy radicals and *meta*-quinones as discrete intermediates. In 1968, he received the annual Professional Progress Award of the local Society of Professional Chemists and Engineers.

During his stay with Humble/Esso, Starnes began to consider the possibility of a career in teaching, which was the family profession. For that reason, he declined a transfer to the Esso laboratories in New Jersey in 1971 and accepted a temporary position in the Department of Chemistry of the University of Texas at Austin, where he taught courses in organic chemistry and collaborated with Dr. Rowland Pettit in organometallic research.

In 1973, Starnes was invited to join Bell Laboratories in Murray Hill, New Jersey. Despite his increasing attraction to academia, this opportunity was too enticing to dismiss, because "Bell Labs" was arguably the finest industrial research establishment in the world at that time.

Starnes remained at Bell Labs as a researcher for 12 years. Much of his work there was directed toward the solution of problems that were related to the structure and stability of poly(vinyl chloride) (PVC), which was used extensively by the Bell System in its telecommunication operations. The following is a partial list of the accomplishments that came from his efforts during this period:

- Invented a reductive dechlorination method for determining the molecular microstructures of PVC and other chlorinated polymers. (This method is still the standard approach throughout the world.)
- Identified the principal structural defects in PVC and elucidated their mechanisms of formation. Established the principal mechanism for chain transfer to the monomer during vinyl chloride polymerization.
- Proved that the thermally labile structural defects in PVC are destroyed by the most effective thermal stabilizers used commercially in this polymer.
- Elucidated the chemical mechanism for the initial stage of the nonoxidative thermal degradation of PVC.
- Proposed and then confirmed that Lewis-acid chemistry is responsible for the action of many of the metallic smoke suppressants and fire retardants used commercially in PVC.

- Established the chemical mechanisms for the formation of aromatic fuel species from PVC during fires.
- Showed that the copolymer of vinyl chloride with carbon monoxide is actually a copolymer of vinyl chloride with acryloyl chloride because of a free-radical rearrangement that occurs during chain propagation.
- Discovered a new type of cyclopolymerization that forms dichlorocyclohexyl branches during copolymerization of vinyl chloride with 1,3-butadiene.

In 1982 Starnes became a member of the first group of scientists to receive the Bell Laboratories Distinguished Technical Staff Award. This group comprised ca. 2 % of the Bell Labs scientific staff.

Stimulated by the federally mandated breakup of AT&T, the parent company of Bell Labs, Starnes finally succumbed to the siren call of academia in 1985 and went to Polytechnic University in Brooklyn, New York, as Head of the Department of Chemistry and Life Sciences. There he taught advanced courses in polymer science and organic chemistry while continuing his research with support from the National Science Foundation and several industrial companies. The research showed that the reductive dechlorination method he had invented could be used to elucidate the molecular microstructures of (vinylidene chloride) – (methyl acrylate) copolymers. It also revealed some unusual features of the smoke suppression of PVC by copper additives and proved that tribasic lead sulfate, a very effective thermal stabilizer for PVC, does not perform that function by destroying structural defects in the polymer.

In 1989 Starnes became the first Floyd Dewey Gottwald, Sr., Professor of Chemistry (a fully endowed Virginia Eminent Scholar chair) at the College of William and Mary, from which he retired to Emeritus status in 2006. There he continued his research with Chemistry students, Ph. D. candidates in Applied Science, postdoctoral associates, and visiting scientists, while teaching courses in polymer science and organic chemistry. Some of his research achievements at William and Mary have been as follows:

- Completed elucidation of the structures, concentrations, and formation mechanisms of all of the structural defects in PVC.
- Identified and quantified a second mechanism for chain transfer to the monomer and thus achieved a full description of the mechanism for vinyl chloride polymerization.
- Disproved mechanisms for the thermal dehydrochlorination of PVC involving ketochloroallyl structural defects, high-energy isotactic conformers, or six-center concerted reactions.
- Proved that the thermal dehydrochlorination of PVC involves a sequential ionic or quasiionic *beta*-elimination that is initiated by internal allylic chloride and

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tertiary chloride structural defects and is autoaccelerated by free radicals formed *in situ* from polyenes and HCl.

- Invented a highly effective new method for the thermal stabilization of PVC without the use of heavy metals (the “Ester Thiol” technology) and established the mechanism of action of the new stabilizers. (A part of this technology has been licensed for commercialization.)

- Showed that certain copper additives are superlative smoke suppressants for PVC and that some of them function through reductive crosslinking chemistry (collaborative work with Dr. Robert D. Pike).

- Established a detailed mechanism for the fire retardance of nylon 6,6 and other polymers by mixtures of antimony trioxide and “Dechlorane Plus”.

- Established the mechanisms of chain transfer to the monomer and to aromatic solvents during the polymerization of vinyl acetate.

- Introduced the use of DDQ as a reagent for the synthesis of polyaniline from aniline monomer.

- Determined the correct structures of the “spiroaminobarbituric acids” that had been studied more than 40 years before (see above).

Starnes’s research in academia has been supported by 22 governmental and private agencies. The research has led to some 510 publications, patents, and presentations that have included guest lectures in 19 countries on 5 continents. An invited historical account of his work on the anomalous structures in PVC has been published [W. H. Starnes, Jr., “Structural Defects in Poly(vinyl chloride)”, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 2451– 2467 (2005)].

The organizer of a number of scientific symposia, including a large international conference on PVC in 2001, Starnes served on the scientific committees or in alternative administrative capacities for many other national and international meetings. He organized and taught several intensive short courses on chlorinated polymers in North America and overseas and was a Distinguished Visiting Professor for the USSR Academy of Sciences (1990), the Russian Academy of Sciences (1992), and the Beijing Institute of Technology (1996). Some of his numerous voluntary activities for the American Chemical Society were membership on the Board of Directors of the Southeastern Texas (Houston) Section, creation of the annual Southeastern Texas Section Award while chairing that section’s Committee on Awards and Nominations, and service as an Executive Committee Member-at-Large and local meeting organizer for the Virginia Section. Some of his other professional responsibilities were the following: Scientific Advisor, European Multinational Environmental Research Project on PVC in Soil and Landfills (1995–1999); Editor-in-Chief, *Journal of Vinyl and Additive Technology*

(1998–); Editorial Board Member for *Polymer Degradation and Stability* (1997–) and several other journals; Chair, Chemistry Subpanel, and Member, Panel on Physical Sciences and Engineering, Project 2061 of the American Association for the Advancement of Science (1985–1986); Charter Member, Virginia Tech Department of Chemistry Advisory Council (1998–); *Wall Street Journal* Opinion Leader Panelist (1995–); Visiting Scientist, Texas Academy of Sciences (1964–1967); he has been the consultant of 43 governmental and private agencies since 1985.

In 2001 Starnes was named by the Plastics Pioneers Association as one of fewer than a thousand individuals worldwide who have had the greatest impact on the history of plastics. His career activities are being chronicled and documented in the Plastics History and Artifacts Program of the Chemical Heritage Foundation. In 1988, he was profiled as a Polymer Science Pioneer by *Polymer News*, and in 2009, he was named a Distinguished Alumni Scholar by Union College. Some of his other honors were the annual Honor Scroll Award of the American Institute of Chemists (New Jersey) (1989), 3 Doctoral Thesis Advisor and Student Paper Mentor national awards from the Society of Plastics Engineers (Vinyl Plastics Division) (1996, 1998, 2007), and the Excellence in Innovation Award of the Hampton Roads Technology Council (2004). He is a member of Phi Kappa Phi, Sigma Xi, and Phi Lambda Upsilon; a Fellow of the American Association for the Advancement of Science (1975), the New York Academy of Sciences (1997), and the Society of Plastics Engineers (2001); and a Life Fellow of the American Institute of Chemists (1977). His award citation from the New York Academy of Sciences stated: “Polymer chemists are unanimous in assessing his work on poly(vinyl chloride) as the standard in the field.”

In 2008 Starnes joined the pioneer Daniel Boone, Academy-Award-winning actor George C. Scott, and other notables, past and present, as a charter inductee into the Southwest Virginia Walk of Fame. The only scientist to be thus honored, he was described in the award citation as “the world’s leading expert in the chemistry of vinyl plastics”.

Since acquiring Emeritus status at the College of William and Mary, Starnes has continued his sponsored research with students at the college and has maintained all of his other professional endeavors except the teaching of formal courses. He and his wife, poet Sofia M. Starnes, have also been involved in a number of philanthropic activities with academic institutions.

Professor William Herbert Starnes, Jr. remains fully engaged with his career in (pure and applied chemistry and polymer science.